

L 139,637

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Process for the manufacture of Low Viscosity Water-Soluble Cellulose Ethers

We, KALLE AKTIENGESELLSCHAFT, a body corporate organised according to the laws of Germany, of 190—196 Rheingastrasse, Wiesbaden-Biebrich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the manufacture of low viscosity water-soluble cellulose ethers.

The technological properties of cellulose ethers to a large extent depend on the viscosities of their solutions. Whereas in the earlier prior art medium viscosity cellulose ethers, i.e. such as have medium molecular weights, have usually been employed, recently also high and low viscosity cellulose ethers have increased in accordance.

Low viscosity cellulose ethers which, in comparison with medium and high viscosity cellulose ethers, also have lower molecular weights, can be produced in two different ways. There is used as starting material either a low-molecular weight alkali cellulose which is etherified, or a cellulose ether which is degraded until it has the desired molecular weight. Both methods have been used in practice but neither is free from objection.

In the production of alkali cellulose having a low-molecular weight, the degradation of cellulose requires very long reaction times or energetic reaction conditions. In this case, the cellulose is exposed particularly intensely to the action of alkali, which results in undesirable discolouration.

Even more substantial is the disadvantage that, after reacting, the alkali cellulose contains a considerable short chain portion which, in the course of the following purifying processes of the cellulose ethers produced therefrom, with water or aqueous solvent mixtures, markedly swells or is completely washed out.

The additional use of oxidizing agents or

catalysts during degradation has not been able to overcome such difficulties.

The second method mentioned of degrading cellulose ethers of higher molecular weights to give low viscosity cellulose ethers of lower molecular weights may be performed by the action of oxidizing agents, such as hypochlorite or hydrogen peroxide. When cellulose ethers which coagulate in hot water are degraded with hydrogen peroxide, conventional processes are employed in a manner such that the cellulose ether is exposed to the oxidizing agent in a hot aqueous suspension, the oxidizing agent being dissolved in the solution, essentially water. An excess of oxidizing agent is used and the degradation of the high-molecular weight cellulose ether is regulated by the time of reaction and the temperature of the medium. In removing the excess of oxidizing agent by washing out the low viscosity cellulose ether, losses of material occur by eliminating the short chain portions. A further disadvantage of such processes resides in that the desired viscosity can be obtained only by interrupting an otherwise continuous process. For this reason, the control of the degradation process is difficult.

The afore-mentioned process is not suitable for degrading cellulose ethers which are soluble in hot water, such as the ionic carboxymethyl cellulose or the non-ionic hydroxyethyl cellulose. But for reacting such ethers, processes are known wherein alcohols are added to the water in order to render the cellulose ethers insoluble.

The present invention is based on the observation that low viscosity water-soluble cellulose ethers can be produced in one operation and without addition of further substances by oxidative degradation with hydrogen peroxide of cellulose ethers having higher viscosities. The process of the invention comprises mixing a cellulose ether having a higher viscosity with a solution of hydrogenperoxide in water only, the mixing ratio being so selected

[Price 4s. 6d.]

that the content of hydrogen peroxide, calculated on the dry cellulose ether, is 0.1 to 10% by weight and the water content of the mixture, calculated on the total, does not exceed 75% by weight, and drying the mixture at temperatures from 100°C to 250°C until the hydrogen peroxide is destroyed to an extent of at least 95%.

According to the process of the present invention, drying and degrading and also destruction of the hydrogen peroxide may be performed in one operation. The molecular weight and thus the viscosity initially decrease very rapidly but reach the final values slowly whereas the loss in moisture and in hydrogen peroxide is almost parallel to the decrease in viscosity. The reaction velocity is determined by the prescribed drying temperature. Under prescribed drying conditions, the degrading effect depends on the quantity of hydrogen peroxide incorporated into the ether. When the reaction is complete, the ether can be used without any further purifying process being necessary.

The process of the present invention can be performed either discontinuously or continuously. Particularly the continuous operating method may easily be included in the usual scheme for the production of cellulose ethers. In this case, the high molecular weight starting material, as produced, is preferably hydroextracted only to a water content of 20 to 55% and thereafter mixed with the aqueous hydrogen peroxide solution. A particularly good distribution of the hydrogen peroxide is thereby obtained.

Suitable starting materials are ionic and non-ionic cellulose ethers, such as carboxymethyl cellulose, methyl cellulose and the mixed ethers derived from methyl cellulose, such as methylhydroxyethyl cellulose or methylhydroxypropyl cellulose.

As mentioned above, it is not absolutely necessary to perform the degradation until the hydrogen peroxide has been completely destroyed. The reaction only needs to be conducted to such an extent that not more than 5% of the originally added hydrogen peroxide is still contained in the marketable product. The remaining hydrogen peroxide decomposes within a few days, without the viscosity of the ether being affected.

Particularly when degrading methyl cellulose, but to a certain extent also when degrading other cellulose ethers, acid products are obtained in side-reactions. They reduce the value of the end product. It has now been found that it is advantageous to neutralize such acid products as they are produced, the reaction mixture being rendered slightly alkaline, advantageously in a manner such that

the reaction product is just neutral. The simplest way to render the reaction mixture alkaline is to treat the hydrogen peroxide solution with sodium carbonate or sodium hydroxide. The alkaline solution and the hydrogen peroxide solution may also be employed separately. The pH value of the alkaline solution which is applied to the cellulose ether having a higher molecular weight should be in the range from 9 to 11. When sodium carbonate is used, the quantity to be employed is between 0.1 and 0.3% by weight, calculated on the dry cellulose ether. It is also possible to incorporate the alkali required together with the cellulose ether in a manner such that the alkali is not completely washed out during the production of the ether.

Mixing the cellulose ethers with the aqueous hydrogen peroxide solution is performed either in portions in mixers or kneaders, or continuously in inclined rotary cylinders or similar devices. Preferably, prior to drying, the friable and moist reaction mixture of cellulose ether and aqueous hydrogen peroxide solution is converted into a granulate, since such a structure is maintained during drying and a particularly flowable product is obtained.

Drying of the mixture granulate can be performed in conventional dryers. Preferably a drum dryer having an air inlet temperature of about 200°C is used.

The low-molecular weight and low viscosity cellulose ethers obtained by means of the process of the present invention show no discoloration and thus are high-quality commercial products.

The following examples illustrate the invention. All figures for viscosity value in centipoises refer to measurement in 2% by weight solution, in water only, at 20°C., using a falling sphere viscometer.

#### EXAMPLE 1

A number of batches of 5 kg of carboxymethyl cellulose (CMC) having a moisture content of about 27% by weight, calculated on the total, and a viscosity as indicated in the following table, were sprayed with 1230 ml of aqueous hydrogen peroxide and kneaded for 30 minutes. Various quantities of hydrogen peroxide were used as set forth in the Table. The quantities are referred to anhydrous carboxymethyl cellulose. The moist substance thus prepared was ground to give a granulate and dried at 110°C in a tumbling dryer until hydrogen peroxide could just no longer be detected. The viscosities of the products obtained are indicated in the right hand column. The reaction time was almost exactly 90 minutes in all cases

TABLE

Batch No.	Initial Viscosity (centipoises)	H <sub>2</sub> O <sub>2</sub> Addition (% by weight)	Final Viscosity (centipoises)
1	440	0.3	76
2	440	0.6	41
3	440	1.2	8
4	3350	1.2	112
5	3350	2.4	54
6	3350	10.0	10

## EXAMPLE 2

20 kg of methylhydroxyethyl cellulose (MHEC) having a methoxyl content of 27%, a hydroxyethyl content of 3% and a water content of 55% by weight, calculated on the total, and a viscosity of 750 cp were combined with 7 litres of aqueous hydrogen peroxide solution in a continuously operating kneader so that the hydrogen peroxide content, calculated on the dry methylhydroxyethyl cellulose, was 1% by weight. The product, in the moist state, was ground to give a flowable granulate and continuously dried in a drum dryer. The retention time was 30 minutes and the inlet temperature of the hot air was 200°C. Only 0.6% of the original quantity of hydrogen peroxide remained. The viscosity of the degraded methylhydroxyethyl cellulose was 25 cp.

When 7 litres of an aqueous hydrogen peroxide solution of only 0.65% by weight were employed but the reaction was performed in the same way, the degraded methylhydroxyethyl cellulose had a viscosity of 80 cp.

## EXAMPLE 3

Methyl cellulose (MC) was degraded. The viscosity of the methyl cellulose was 10500 cp and the water content 50% by weight, calculated on the total. The quantity of hydrogen peroxide employed (calculated on dry MC) and also the viscosity of the degraded methyl cellulose are shown in the following table. The reaction conditions corresponded to those of Example 2. In no case was more than 0.8% of the added hydrogen peroxide left undecomposed.

TABLE

Batch No.	H <sub>2</sub> O <sub>2</sub> Addition (% by weight)	Final Viscosity (centipoises)
1	0.7	2240
2	1.0	120
3	2.0	40

## EXAMPLE 4

Under the same reaction conditions as in Examples 2 and 3, methylhydroxypropyl cellulose (MHPC) having a viscosity of 750 cp and a moisture content of 45% by weight was degraded with aqueous hydrogen peroxide solution. The quantity of hydrogen peroxide used was 1.3% by weight, calculated on the dry substance. The end product had a viscosity of 18 cp. 0.4% of the added hydrogen peroxide remained.

The total weight per cent of water present

in the starting mixtures of the above Examples can be calculated or approximately from the data given, using a table of densities of hydrogen peroxide. In all cases the figure is less than 75%.

## WHAT WE CLAIM IS:—

1. A process for the manufacture of low viscosity water-soluble cellulose ethers, wherein a cellulose ether having a higher viscosity is mixed with a solution of hydrogen peroxide in water only, the mixing ratio being so selected that the content of hydrogen peroxide,

- calculated on the dry cellulose ether is 0.1 to 10% by weight and the water content of the mixture, calculated on the total, does not exceed 75% by weight, and the mixture is then dried at temperatures of 100 to 250°C until the hydrogen peroxide is destroyed to an extent of at least 95%.
2. A process as claimed in claim 1, wherein a cellulose ether starting material having a water content of 20 to 55% by weight, calculated on the total, is employed.
3. A process as claimed in claim 1 or 2, wherein the reaction mixture is rendered alkaline by mixing the cellulose ether starting material with an aqueous solution having a pH value of 9 to 11 and in which the required hydrogen peroxide may be dissolved.
4. A process as claimed in any one of claims 1 to 3, wherein prior to drying, the mixture of cellulose ether starting material, water, hydrogen peroxide and, if desired, alkali or alkali carbonate, is converted into a granulate.
5. A process as claimed in any one of claims 1 to 4, wherein the operation of granulating, if desired, and drying are performed continuously in that sequence.
6. A process as claimed in claim 1, substantially as described in any one of the Examples herein.
7. Low viscosity water-soluble cellulose ethers, when made by the process claimed in any one of claims 1—6.

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